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FACULTY OF ENGINEERING AND ARCHITECTURE

Relumped Single-Event MicroKinetic Model for Aromatics Hydrogenation on Pt Catalyst

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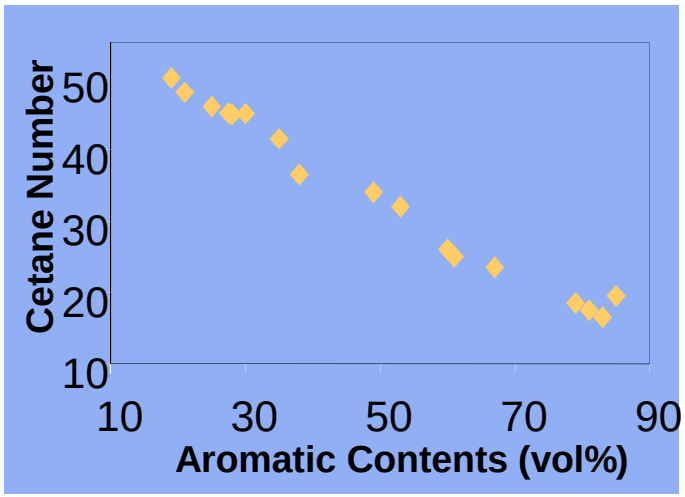
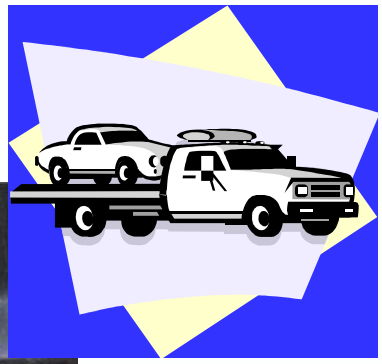
ERIC European Research Institute of Catalysis

aromatics hydrogenation

- fuel quality: cetane number for diesel
  smoke point for jet fuel





- environmental: carcinogenic character

- industrially: cyclohexane from benzene
  hydrogenation, a base chemical of nylon

(relumped) microkinetics

- fundamental understanding
  - model compounds
  - detailed analyses
  - extended computation times

microkinetics vs. lumped kinetcs

'relumped' microkinetics

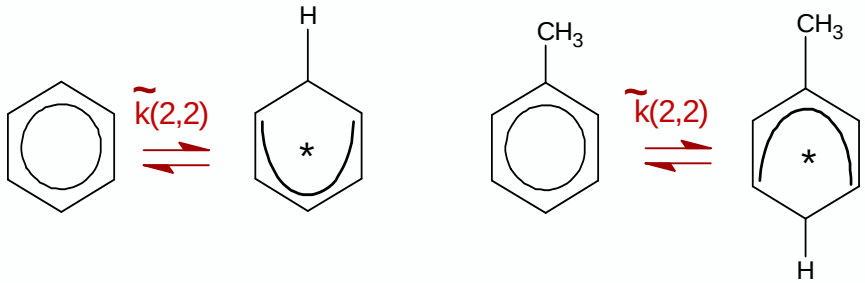
- real-life applications
  - global characterization
  - fast feedback loops

outline

- introduction
- SEMK model for aromatics hydrogenation
  - single-event concept
  - benzene hydrogenation on Pt
- relumped SEMK microkinetics
  - potentially dominant reaction pathways
  - lumping coefficients
  - relumped model performance
- conclusions

Single-Event MicroKinetics (SEMK)

- large number of species and elementary steps
- limited number of reaction families defined based on (energy/enthalpy)
  - reaction type
  - types of intermediates involved
- accounting for symmetry effects (entropy)



$$k(m,n) = \frac{\sigma^{reactant}_{global}}{\sigma^{\#}_{global}} \frac{k_b T}{h} \exp\left(\frac{\Delta \tilde{S}^{0,\#}}{R}\right) \exp\left(-\frac{\Delta H^{0,\#}}{RT}\right) = n_e \tilde{k}(m;n)$$

hydrogenation elementary steps

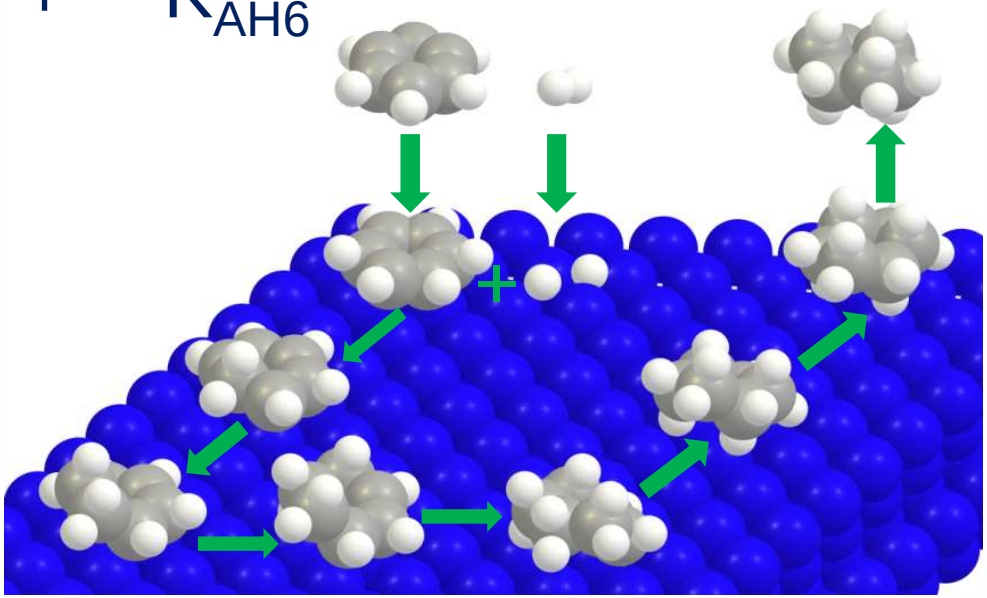
- Horiuti-Polanyi mechanism

$H_2(g) + 2\,* \rightleftharpoons 2\,H^*$ $\quad K_{H2}$

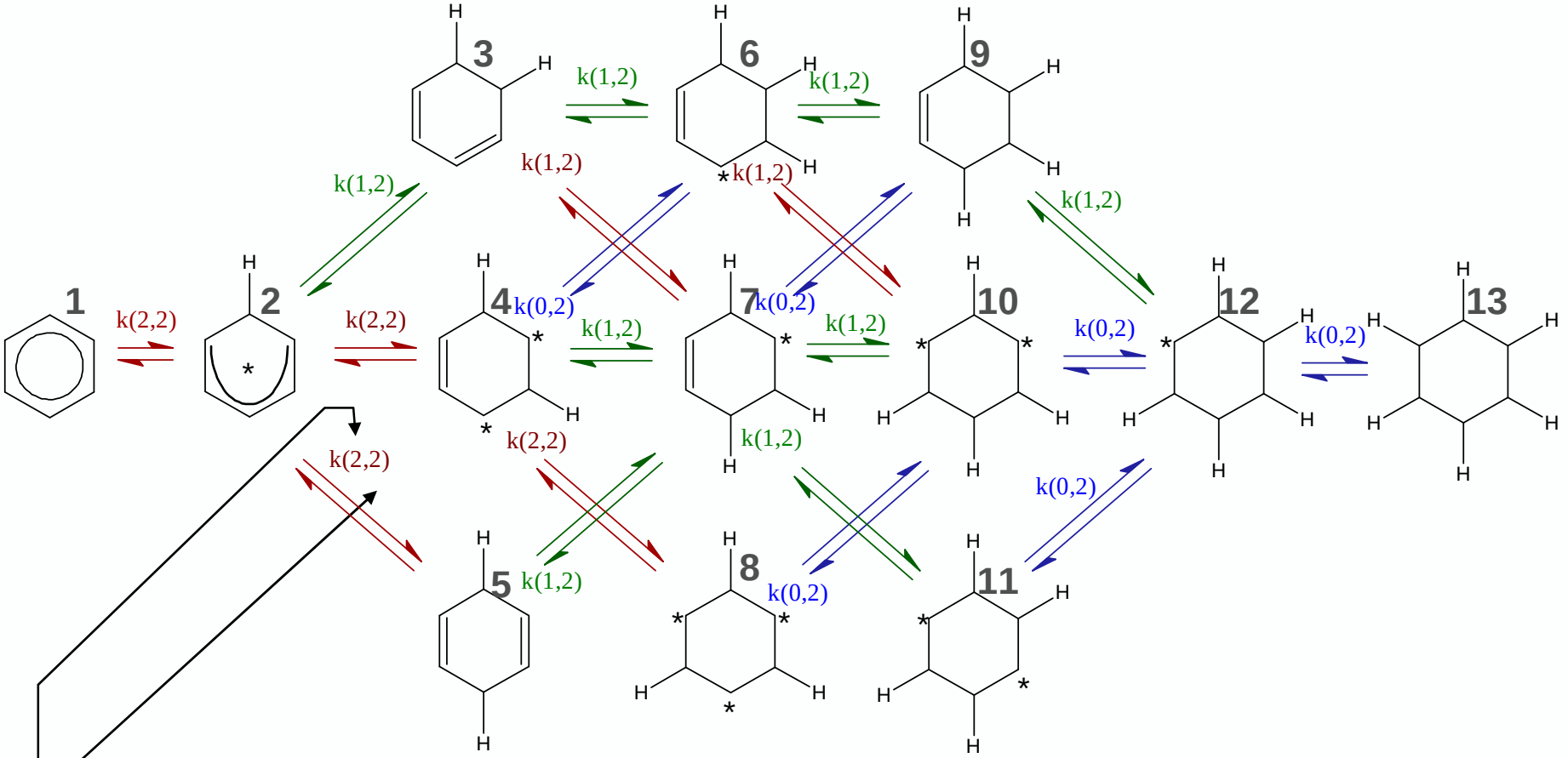
$A(g) + * \rightleftharpoons A^*$ $\quad K_A$

$AH_i^* + H^* \rightleftharpoons AH_{i+1}^* + *$ $\quad K_{i+1}$ $\quad (i=0,..5)$

$AH_6^* \rightleftharpoons AH_6(g) + *$ $\quad K_{AH6}$



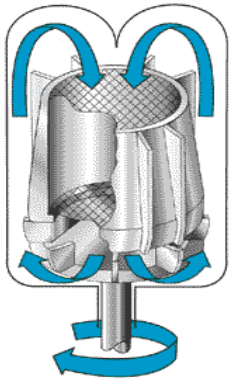
reaction families



- branching degree
- number of unsaturated nearest neighbors

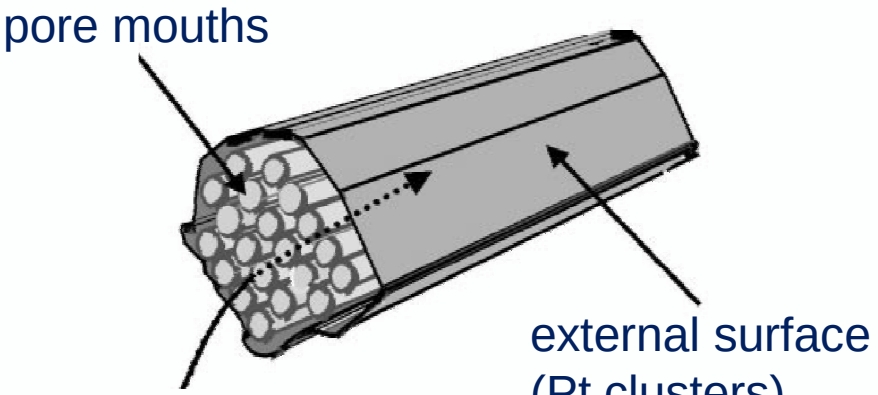
Saeys et al. J. Phys. Chem. B, (2005)

experimental

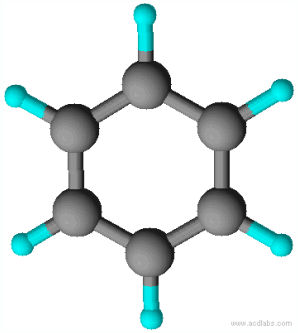


Berty-reactor:

- gas phase
- perfectly mixed
- continuous flow



$$F_{j,out} - F_{j,in} = R_j W$$



p_{tot} (MPa)	T (K)	p_{aro} (kPa)	p_{hyd} (kPa)	space time (kg_{cat} s mol^{-1})
1 – 3	423 – 498	10 – 60	100 – 600	20-70

Thybaut et al. Chem. Eng. J., (2002)

rate equations

$$R_j = \sum_i r_{i\rightarrow j}^{hyd/deh} - r_{j\rightarrow i}^{deh/hyd}$$

i,j: metal chemisorbed cyclic hydrocarbons

$$R_j = \sum_i \begin{pmatrix} n_{e,i\rightarrow j}\left[\tilde{k}_{hyd}(m_i,n_i)C_{H^*} + \tilde{k}_{deh}(m_i,n_i)C_*\right]C_i \\ -n_{e,j\rightarrow i}\left[\tilde{k}_{hyd}(m_i,n_i)C_{H^*} + \tilde{k}_{deh}(m_i,n_i)C_*\right]C_j \end{pmatrix}$$

C_i, C_{H^*} and C_* obtained from:

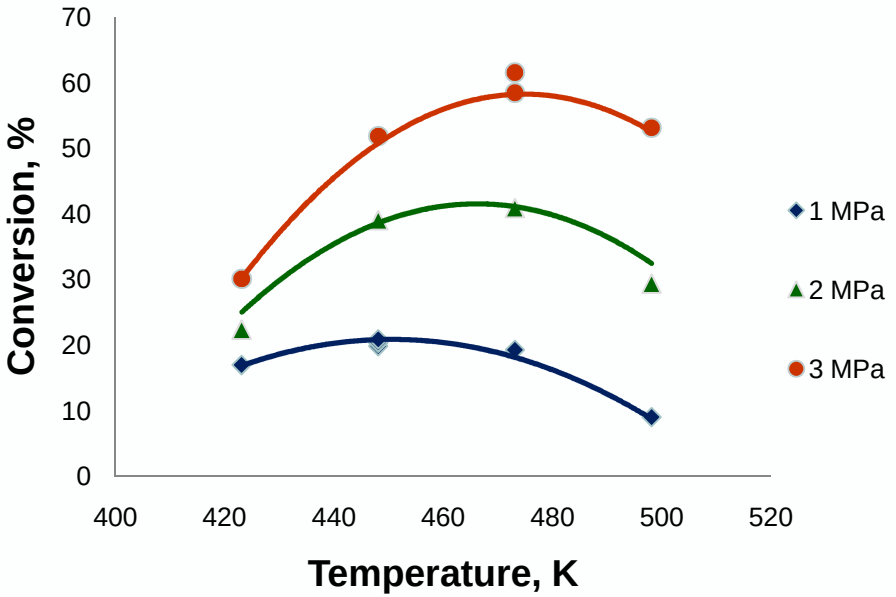
- chemisorption equilibria for aromatic, hydrogen and cyclohexane
- pseudo steady state approximation for all other metal chemisorbed cyclic hydrocarbons
- site balance

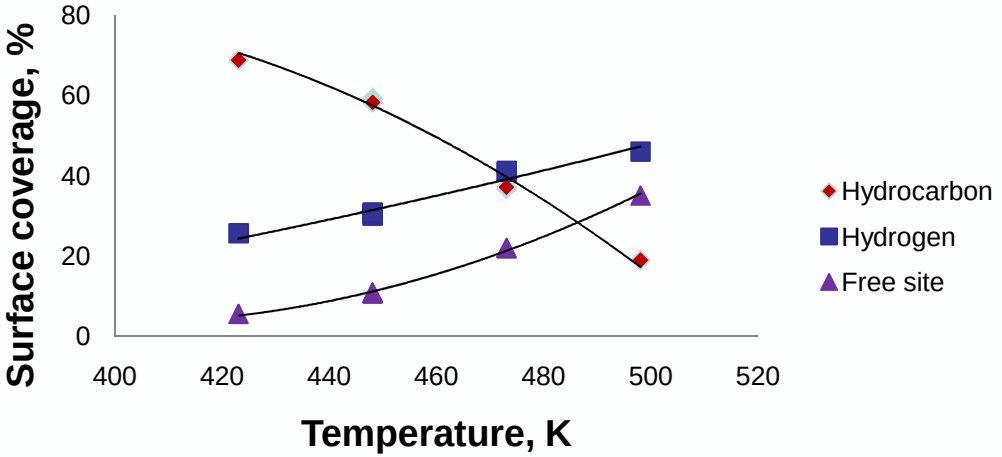
set of n_{int}-2 equations

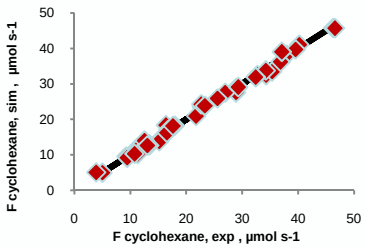
= 13 for benzene, 40 for toluene and 36 for o-xylene

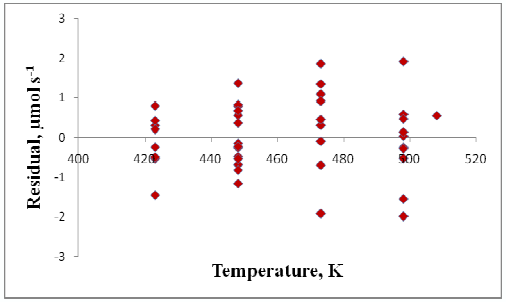
modeling results

Parameter	value (kJ mol^{-1})
$E_a(0,2)$	57.5 ± 0.5
$E_a(1,2)$	65.1 ± 1.9
$E_a(2,2)$	57.5 ± 0.5
$\Delta H(0,2)$	7.9 ± 0.4
$\Delta H(1,2)$*	4.5
$\Delta H(2,2)$	1.2 ± <0.5
ΔH_B	-56.0 ± <0.5
ΔH_{H2}	-59.4 ± <0.5
ΔH_{CHA}*	5.3
F value	4150







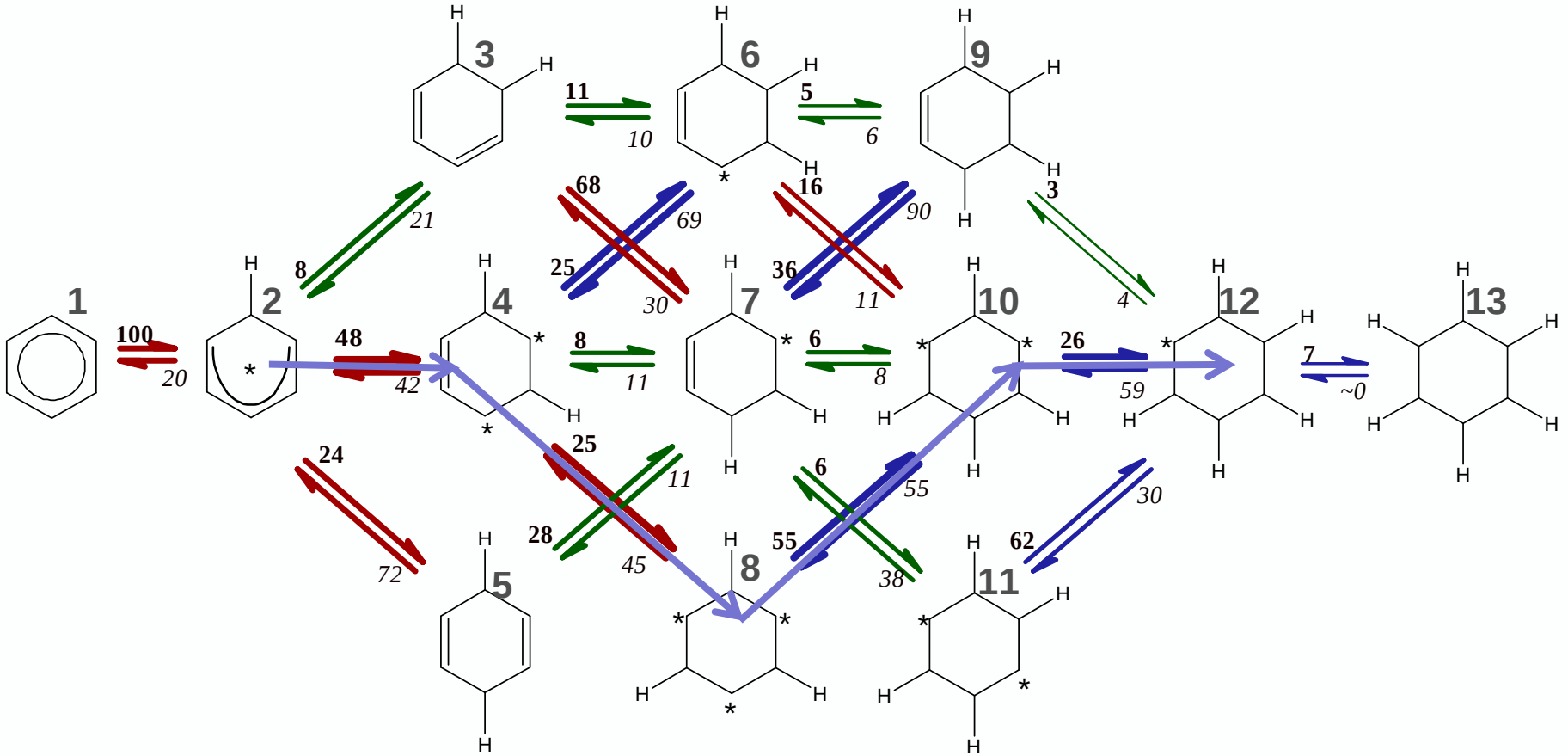


Bera et al. I&ECR, (2011)

Bera et al. ACS Catal., (2012)

reaction path analysis

- numbers indicate % contribution of disappearance of species
- thickness of the arrows corresponds to the order of magnitude of rates
- **hydrogenation** / *dehydrogenation*



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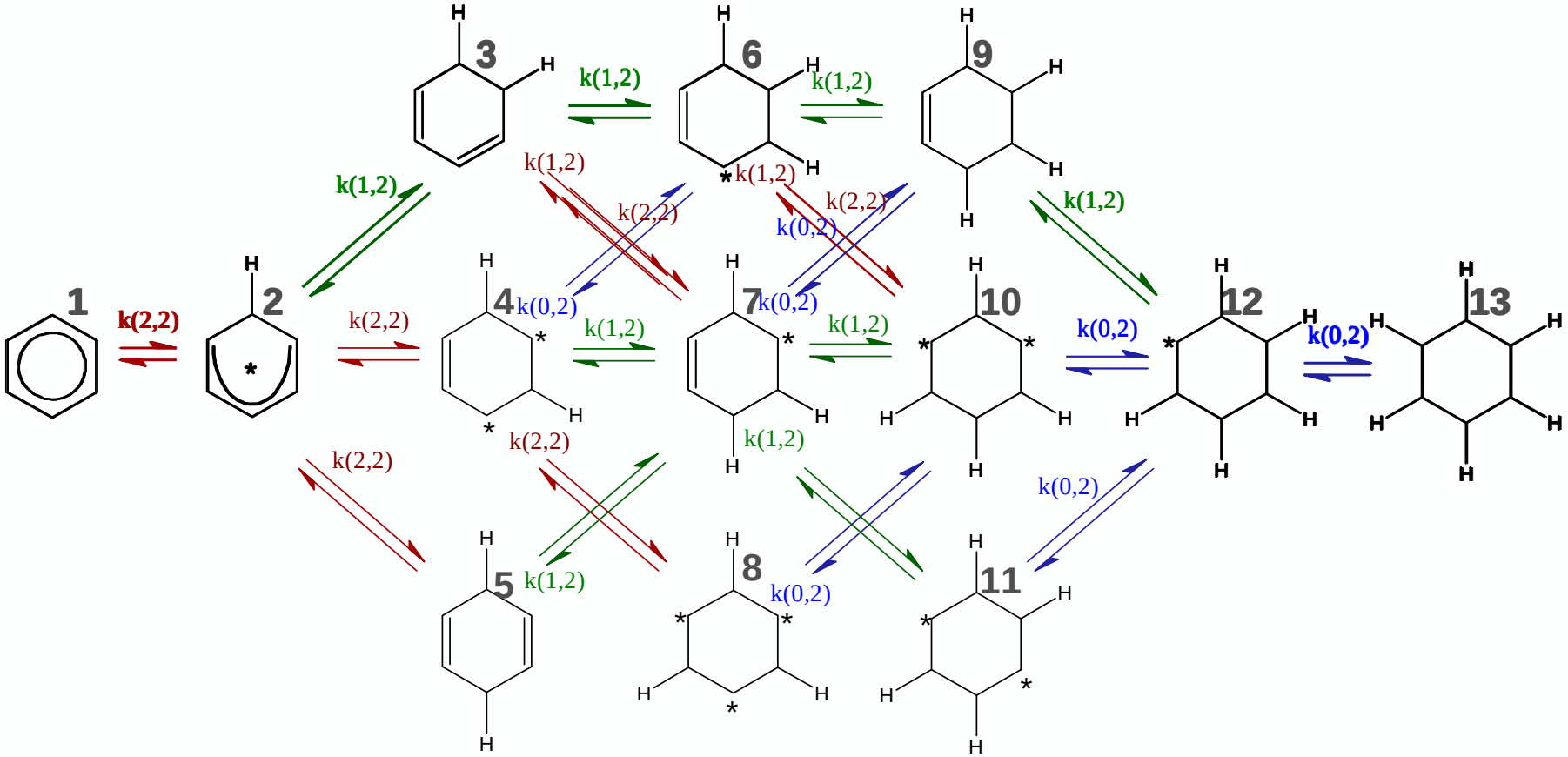
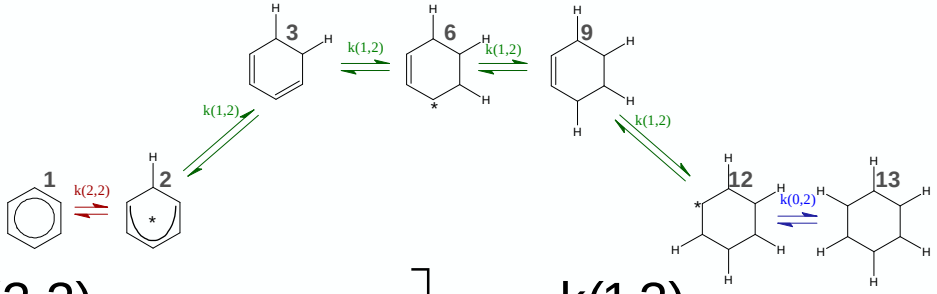
potentially dominant reaction pathways



- 14 ‘forward’ pathways contributing to hydrogenation

rate along a pathway

$$R_{AH_6(g),p} = C_t k(0,2)\theta_{12^*}\theta_{H^*} - C_t \frac{k(0,2)}{K(0,2)}\theta_{13^*}$$



intermediates: $$0 = k(2,2)\ \theta_{H^*}\theta_{1^*} - \left[\frac{k(2,2)}{K(2,2)}\theta_* + k(1,2)\ \theta_{H^*}\right]\theta_{2^*} + \frac{k(1,2)}{K(1,2)}\ \theta_*\theta_{3^*}$$

chemisorption: $$\theta_{1^*} = \theta_* K_A p_A \qquad \theta_{H^*} = \theta_* \sqrt{K_{H_2} p_{H_2}}$$

site balance: $$1 = \theta_* + \theta_{H^*} + \theta_{1^*} + \theta_{2^*} + \theta_{3^*} + \theta_{6^*} + \theta_{9^*} + \theta_{12^*}$$

$$R_{AH_6(g),p} = C_t k(0,2) \frac{B^5(1,2)K(2,2)K(0,2)k(1,2)k(2,2)\sqrt{K_H p_H}K_B p_B}{K(0,2)\left[\left\{\begin{array}{l} B^5(1,2)K(2,2)k(1,2) \\ +\left\langle\begin{array}{l} B^4(1,2)k(2,2) + B^3(1,2)k(2,2) + \\ B^2(1,2)k(2,2) + B(1,2)k(1,2) \end{array}\right\rangle K(1,2) \end{array}\right\} k(0,2) \right.} \theta_*^{\,2}$$
$$\left. + K(1,2)k(1,2)k(2,2) \right]$$

with $$B(1,2) = K(1,2)\theta_{H^*}/\theta_* = K(1,2)\sqrt{K_{H_2} p_{H_2}}$$

relumped reaction rate

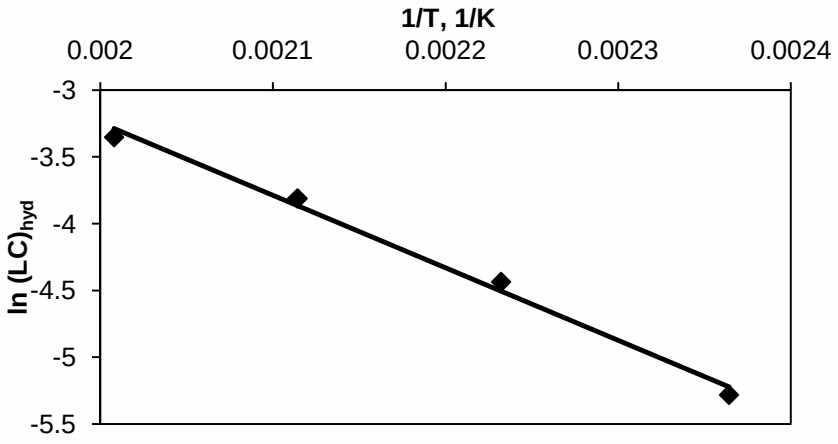
$$R_{CHA(g)} = (LC)_{hyd} \sum_{p} R_{CHA(g),\,p}$$

- lumping coefficients account for
  - different nr. of hydrocarbon species in site balance (7 vs 13)
  - variations in relative surface concentrations

$$(LC)_{hyd} = \frac{7}{13} e^{\frac{-\Delta H_{correction}}{R}}$$

$$\Delta H_{correction} = 13\ kJ\,mol^{-1}$$

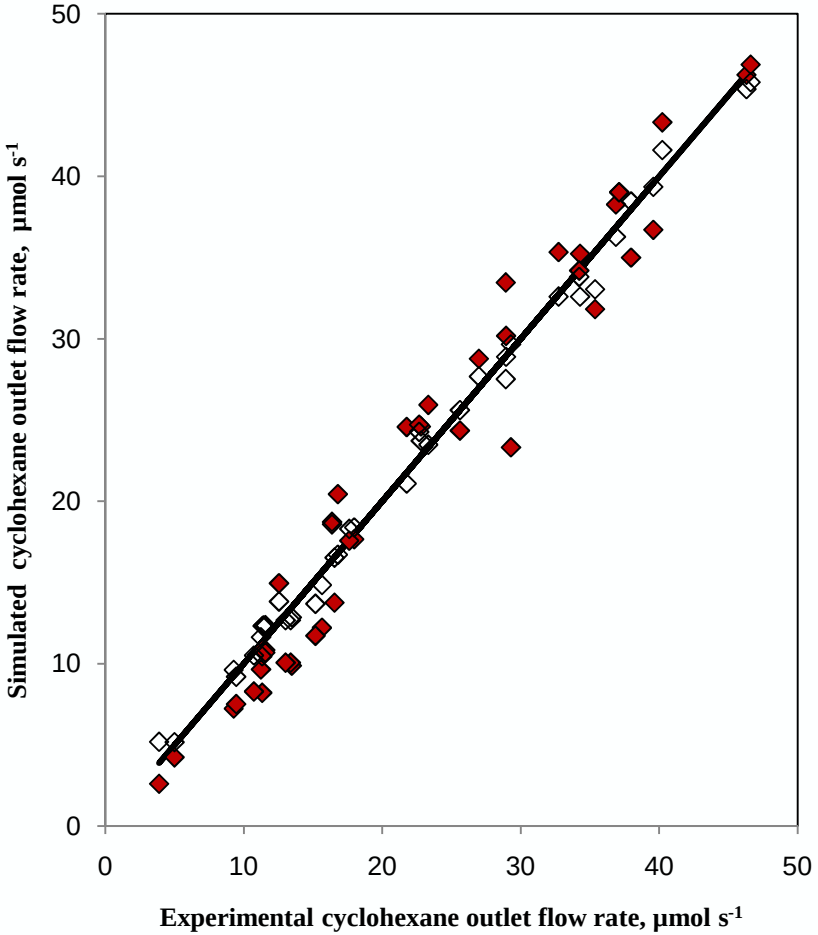
surface thermodynamics correction factor

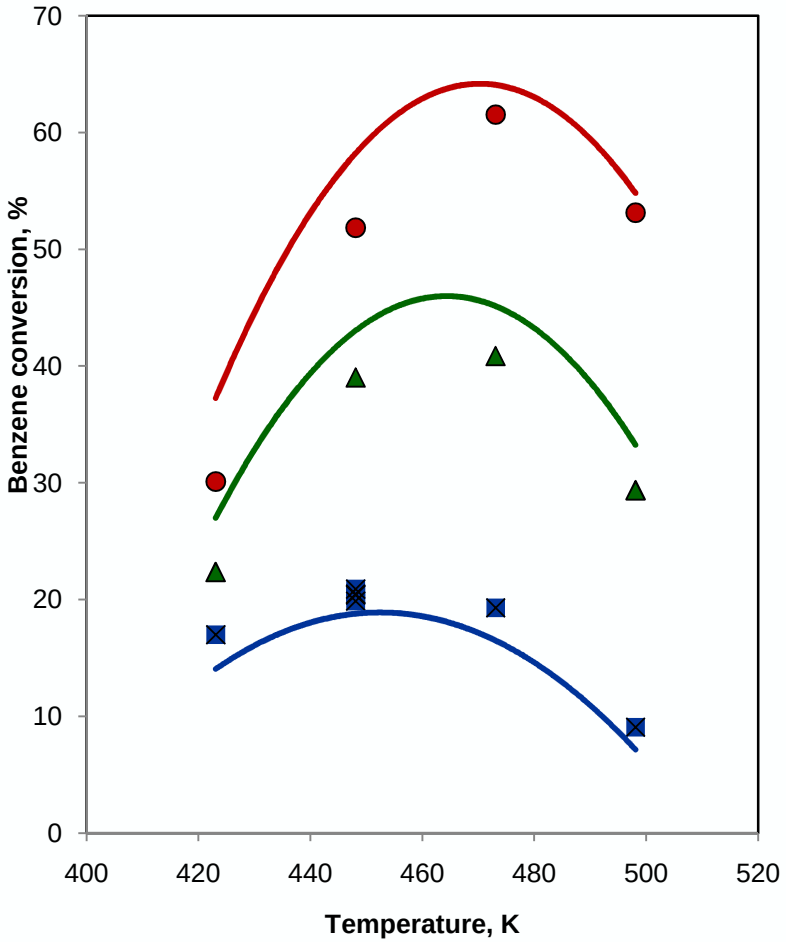


surface intermediates concentrations

Temperature, K	Free site (%)		Hydrogen (%)		Total hydrocarbon (%)		Benzene (%)		Cyclohexyl (%)	
	Rel	Det	Rel	Det	Rel	Det	Rel	Det	Rel	Det
423	6.4	5.7	29.6	25.3	64	69	0.8	0.8	2.6	3.6
448	14.5	11.8	42.1	32.3	43.4	55.8	0.7	0.7	1.2	1.5
473	27	24.6	51	44.6	21.4	30.8	0.7	0.6	0.3	0.4
498	39.4	37.9	51.6	48.4	9	15.9	0.5	0.5	0.1	0.1

relumped model performance

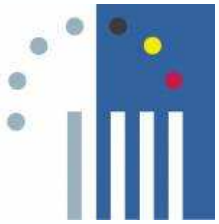




conclusions

- relumped SEMK model for aromatic hydrogenation adequately describes benzene data on Pt
- sum of rates of potentially dominant reaction pathways
- lumping coefficients account for
  - different number of hydrocarbon surface species in pathway
  - surface thermodynamics correction

Acknowledgements



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